Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Bifunctional metal-organic frameworks for hydrogenation of nitrophenol using methanol as hydrogen source

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Supporting information

UiO-66(Zr)-H: $ZrCl_4$ (0,466 g, 2mmol) and terephthalic acid (0,332 g, 2mmol) in 6 ml of *N,N'*-dimethylformamide (DMF) were introduced in a vial. The mixture was sonicated for 20 min. When a homogeneous suspension was formed, the mixture was transfer to a Teflon-lined autoclave, sealed and placed in a pre-heated oven at 220 °C, maintaining the temperature for 12 h.
After this time, the resulting white solid was filtered and washed several times with DMF and methanol. The solid was dried under vacuum at 120 °C overnight.

UiO-66(Zr)-NH$_2$: The synthesis of Zr-NH_2 MOF was carried out dissolving the metallic salt $ZrCl_4$ (0.466 g, 2 mmol) and the organic linker 2-amino-terephthalic acid (0.362g, 2 mmol) in *N,N'*-dimethylformamide (DMF) (6.0 mL, 340 mmol) at room temperature, sonicated for 20 min. The mixture was transferred in a Teflon-lined autoclave, sealed and placed in a pre-heated oven at 100℃ for 24 hours. After cooling to room temperature, the resulting yellow solid was filtered and washed several times with DMF and methanol and dried at room temperature.

UiO-66(Zr)-NO$_2$: The material was synthetized dissolving, in a vessel vial, 0.466g (2mmol) of $ZrCl_4$, 0.422g (2mmol) of 2-nitroterephtalic acid in 6 mL of *N,N'*- dimethylformamide. The resulting mixed solution was sonicated for 20 minutes; subsequently the homogeneous system was transfer in a Teflon-line autoclave that was sealed and placed in a pre-heated oven at 220°C for 24 h. The resulting dark-yellow solid was collected by filtration and washed several times with DMF and methanol. The solid was dried at room temperature and characterized.

MIL-125(Ti)-NH$_2$ was prepared following a previously reported procedure. In a 30 mL vessel vial was introduced a suspension of 2-aminoterephthalic acid (1.43 g, 7.9 mmol) in 20 mL of anhydrous DMF. Then, methanol (5 mL) was added to the flask and the system was sonicated for 20 min. Before transferred the mixture to a 50 mL Teflon-lined autoclave titanium isopropoxide (1.36 g, 4.8 mmol) was added. The autoclave was sealed and heated up to 110 °C for 72 h. After cooling to room temperature, the product was obtained by filtration and in a second moment washed by suspending the powder in DMF for 12 h. Subsequently, the solid was washed with additional DMF at 60 °C for 12 h. This washing procedure was repeated using methanol as solvent to remove the DMF. The material was collected by filtration and dried overnight in an oven at 100 °C.

Figure S1. Photograph of the catalytic device employed for the tandem reaction.

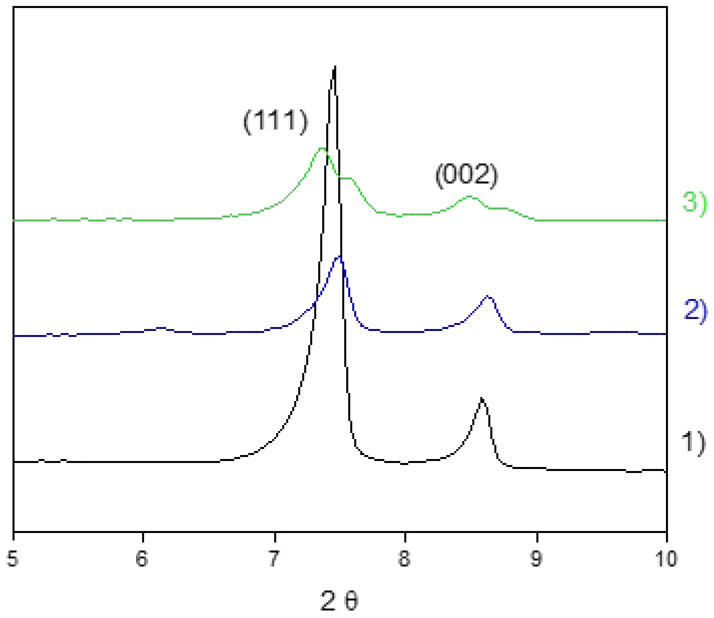

Figure S2. Magnification of the PXRD patterns of UiO-66(Zr)-H (1), UiO-66(Zr)-NH_2 (2), UiO-66(Zr)-NO_2 (3) to mark the difference in the the main peak.

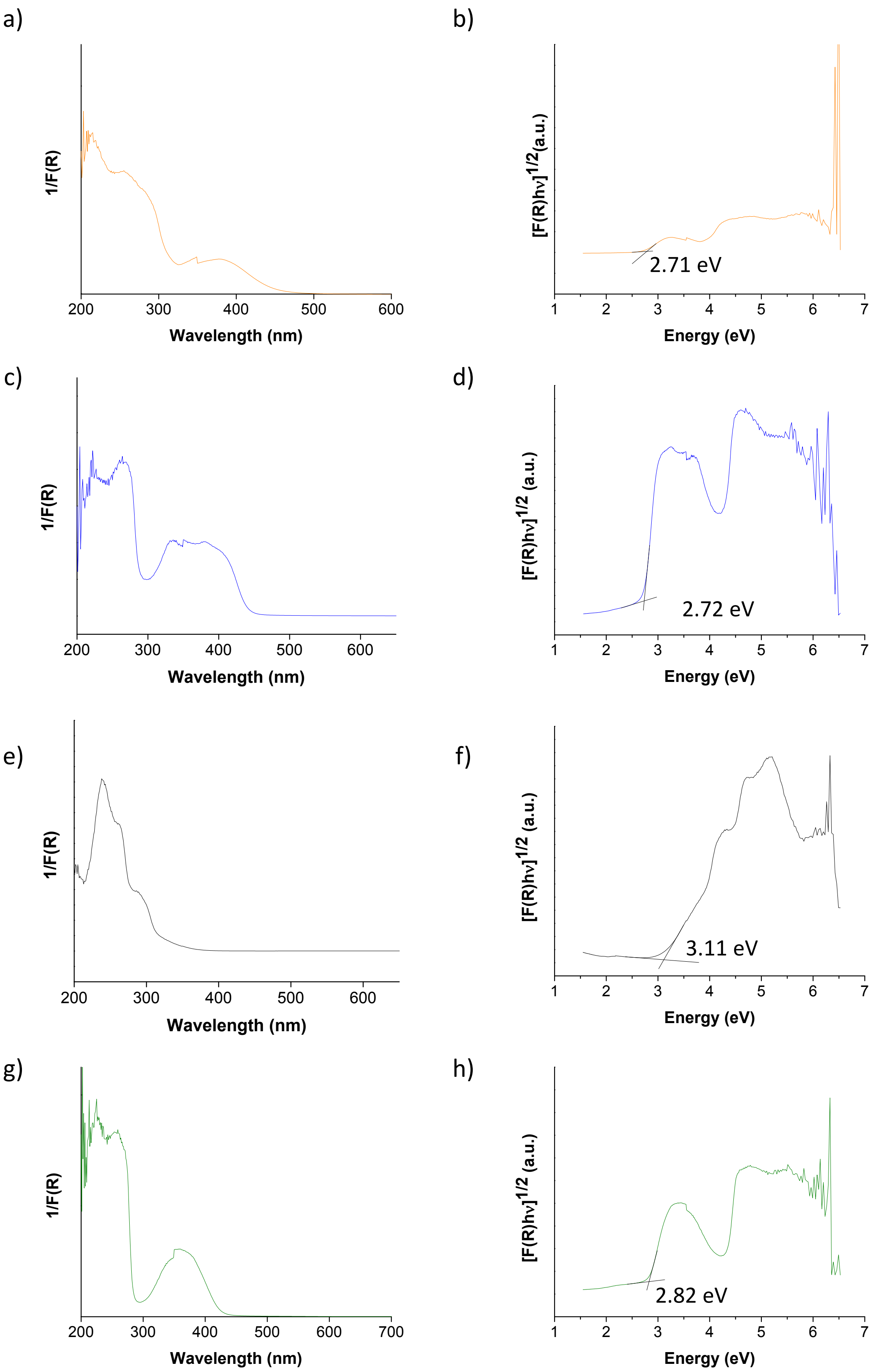

Figure S3. Diffuse UV-Vis (a, c, e) and Tauc plot (b, d, f) for MIL-125(Ti)-NH_2 (a, b), UiO-66(Zr)-NH_2 (c, d), UiO-66(Zr)-H (e, f) and UiO-66(Zr)-NO_2 (g, h).

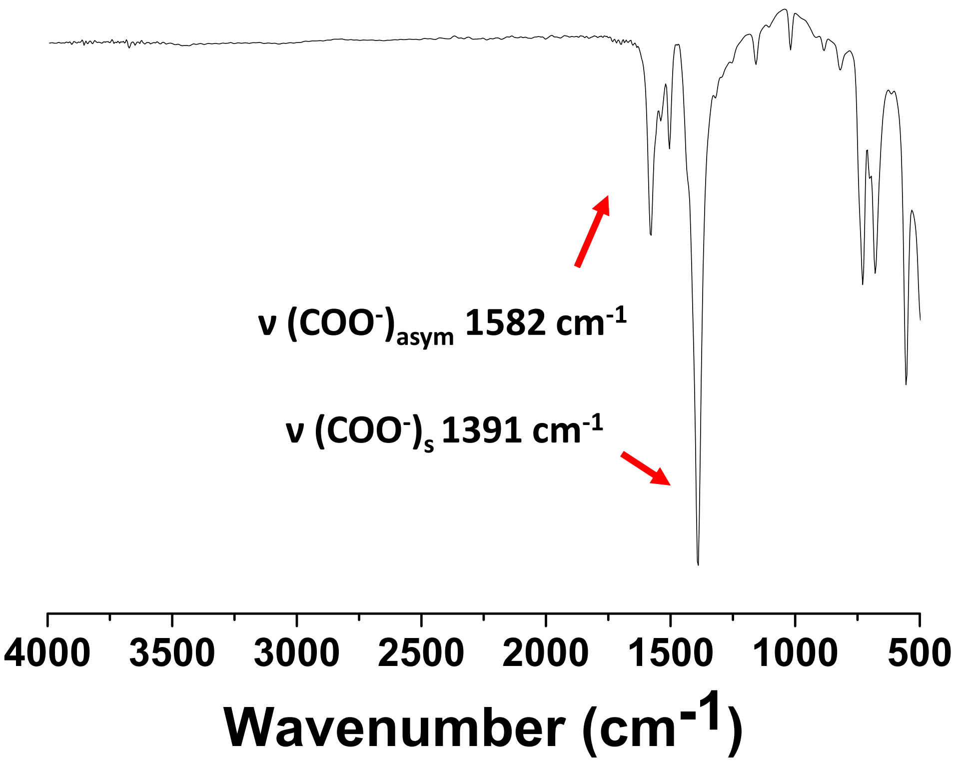

Figure S4. ATR-FT-IR spectrum recorded for UiO-66(Zr)-H.

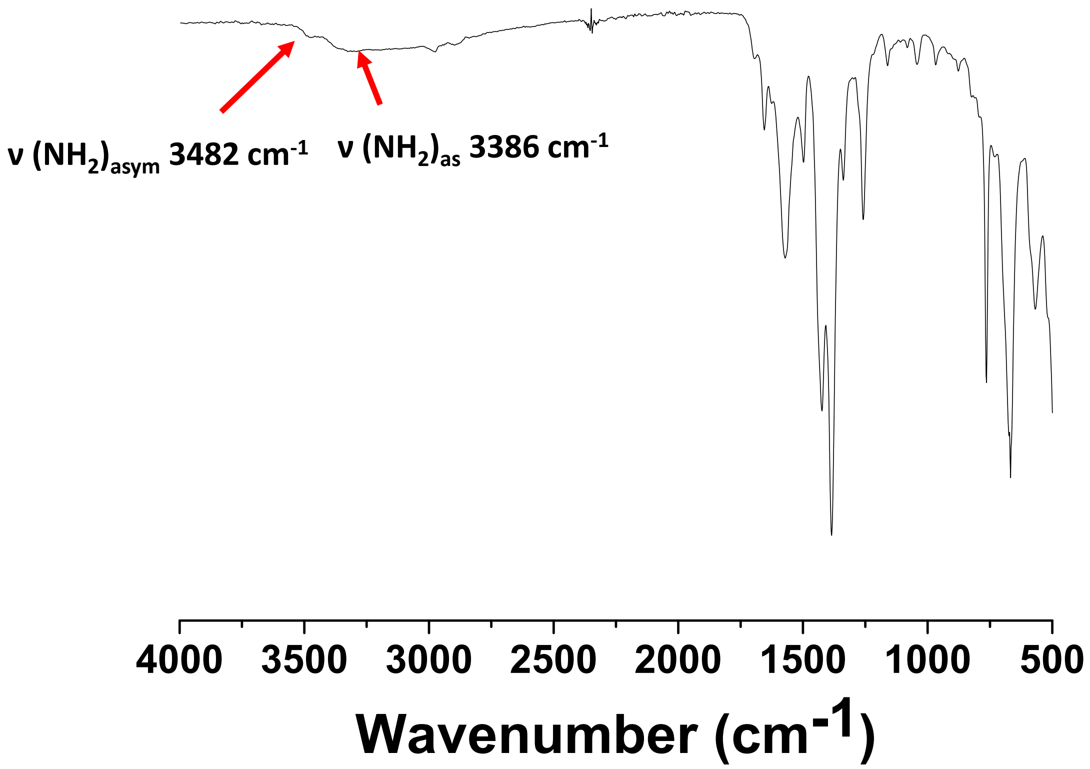

Figure S5. ATR-FT-IR spectrum recorded for UiO-66(Zr)-NH$_2$.

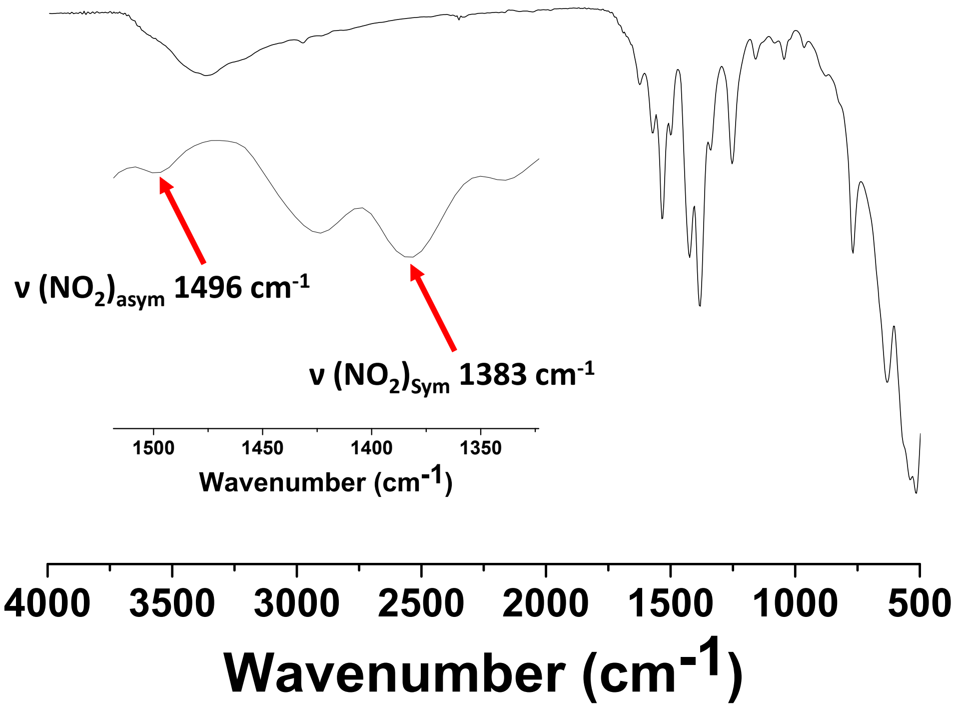

Figure S6. ATR-FT-IR spectrum recorded for UiO-66(Zr)-NO$_2$. The inset shows an expansion of the 1575-1325 cm^{-1} region.

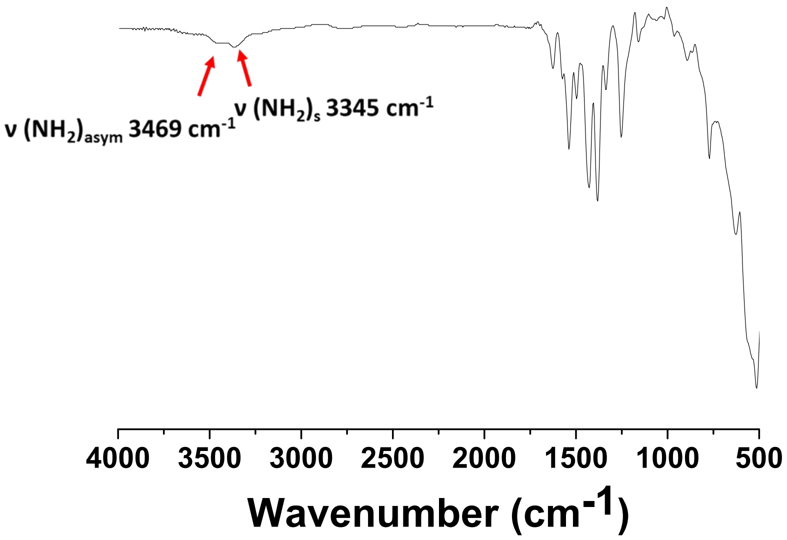

Figure S7. ATR-FT-IR spectrum recorded for MIL-125(Ti)-NH$_2$. The inset shows an expansion of the 1575-1325 cm^{-1} region.

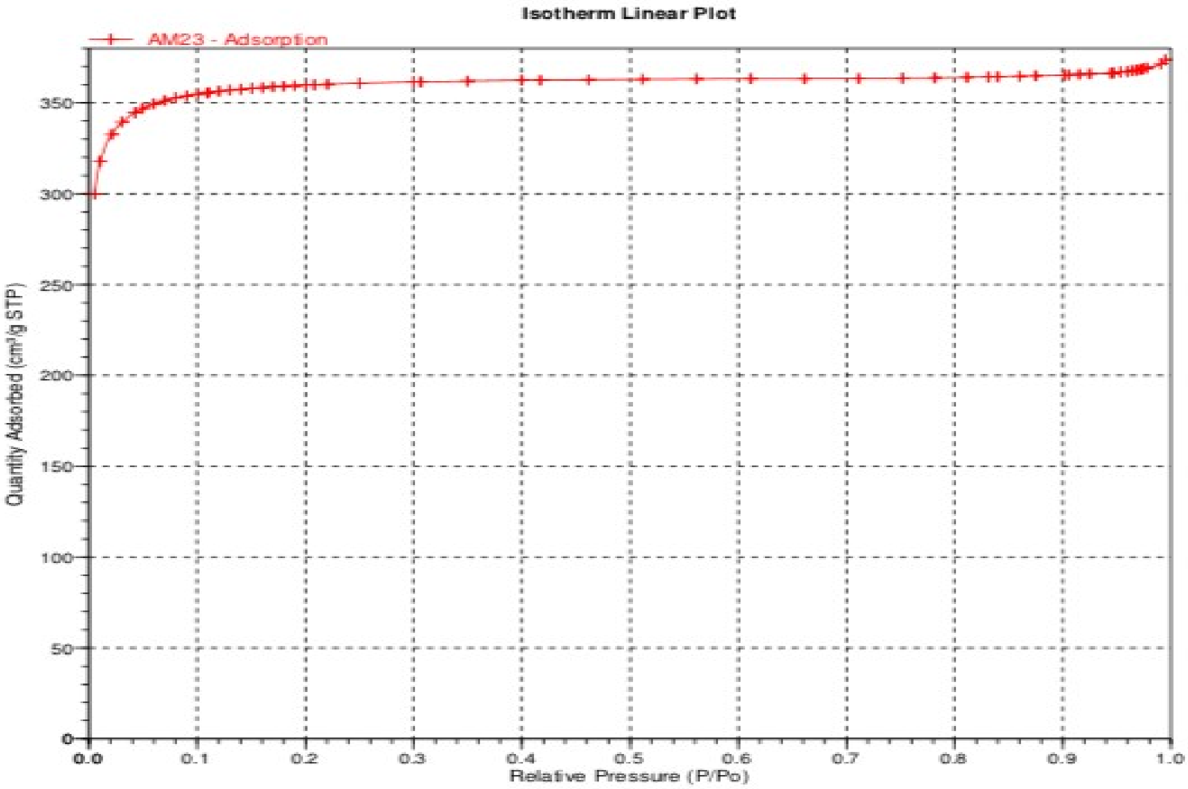

Figure S8. Isothermal N_2 adsorption at 77 K for MIL-125(Ti)-NH_2

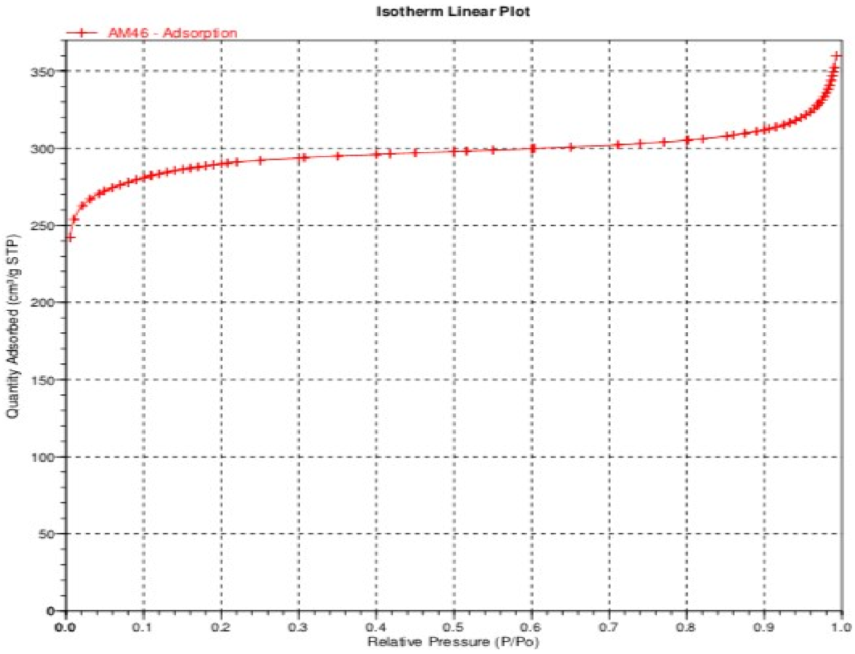

Figure S9. Isothermal N_2 adsorption at 77 K for UiO-66(Zr)-NH_2.

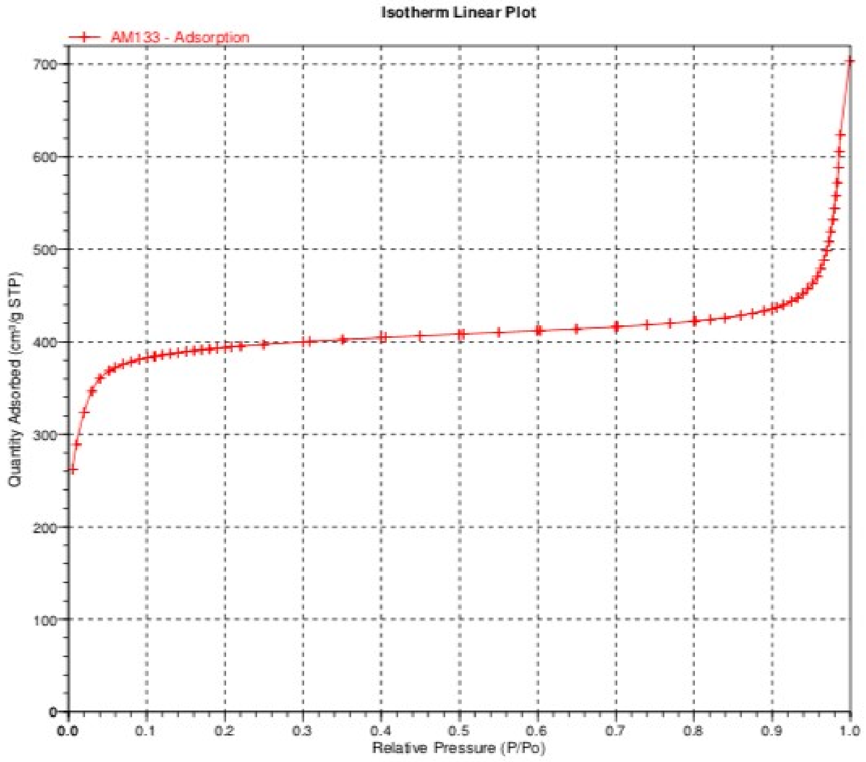

Figure S10. Isothermal N_2 adsorption at 77 K for UiO-66(Zr)-H

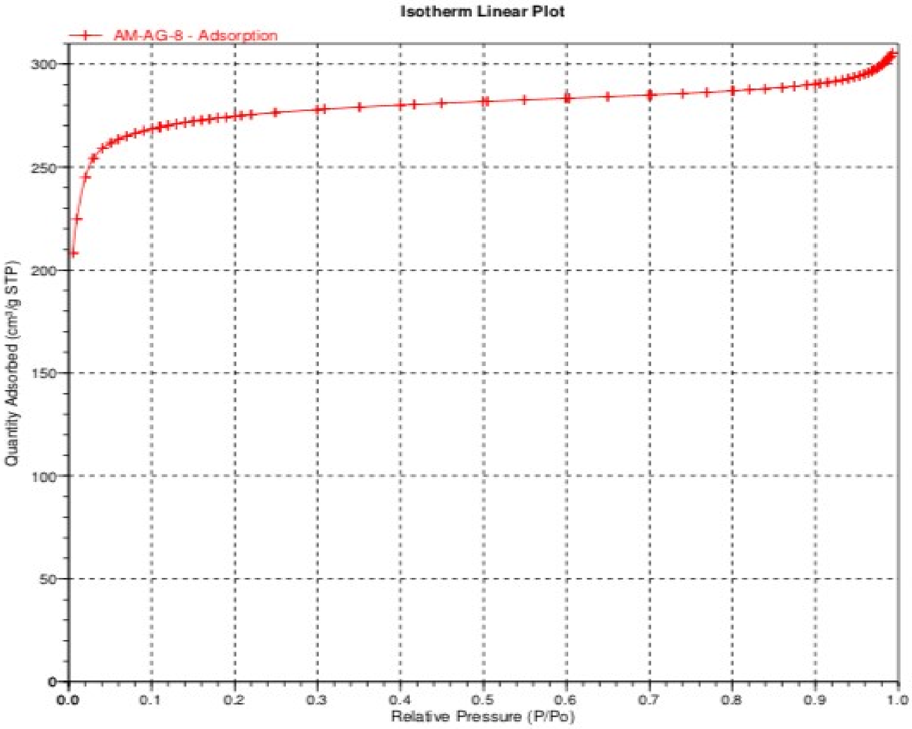

Figure S11. Isothermal N_2 adsorption at 77 K for UiO-66(Zr)-NO_2

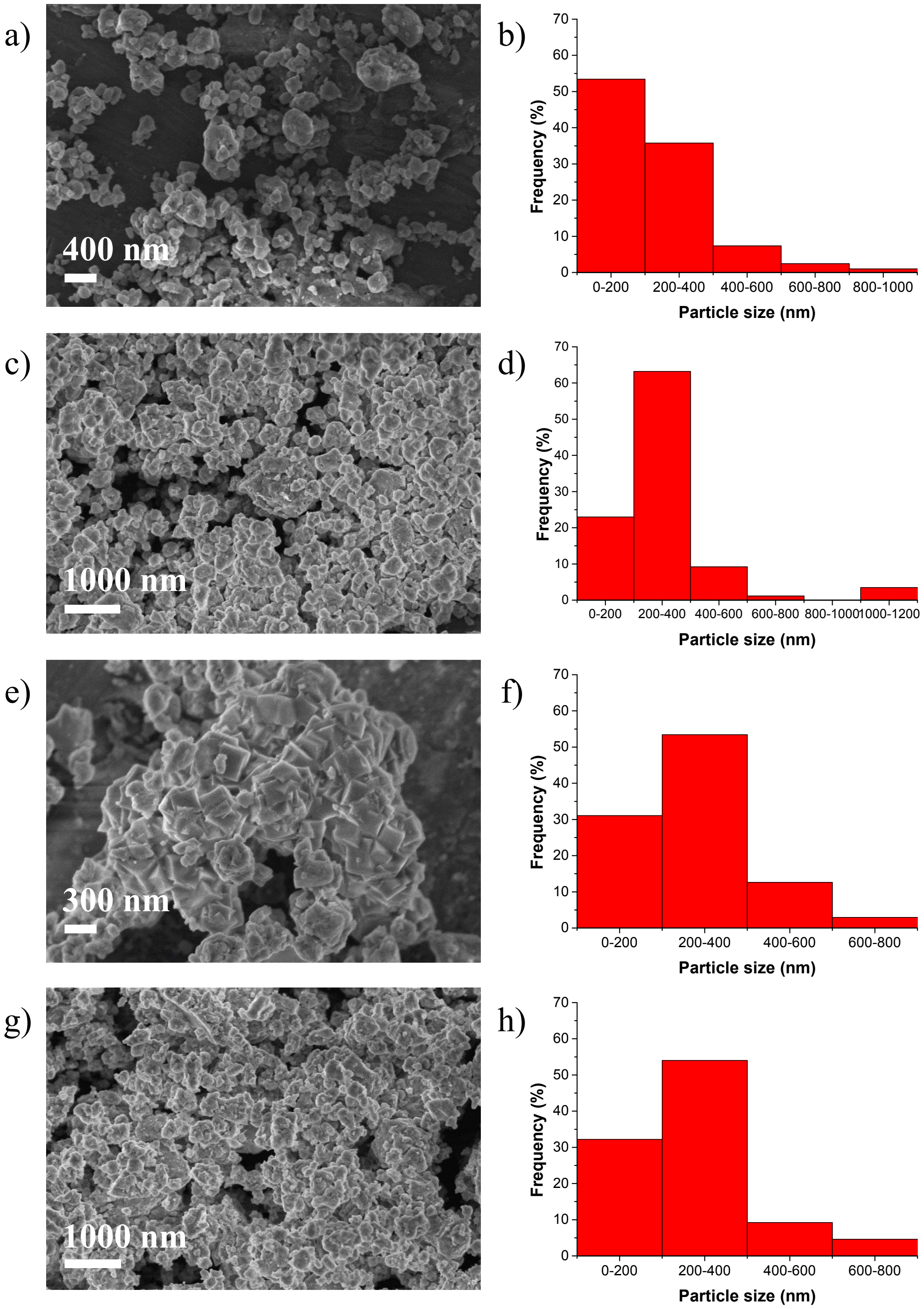

Figure S12. Representative HRSEM images and particle size distribution for MIL-125(Ti)-NH2 (a-b), UiO-66(Zr)-NH_2 (c-d), UiO-66(Zr)-H (e-f) and UiO-66(Zr)-NO_2 (g-h) materials.

Table S1. Summary of the average particle size and standard deviation of the MIL-125(Ti)-NH_2, UiO-66(Zr)-NH_2, UiO-66(Zr)-H or UiO-66(Zr)-NO_2 materials.

Entry	Catalyst	Average particle size distribution (nm)
1	MIL-125(Ti)-NH_2	225 ± 143
2	UiO-66(Zr)-NH_2	304 ± 178
3	UiO-66(Zr)-H	274 ± 112
4	UiO-66(Zr)-NO_2	272 ± 129

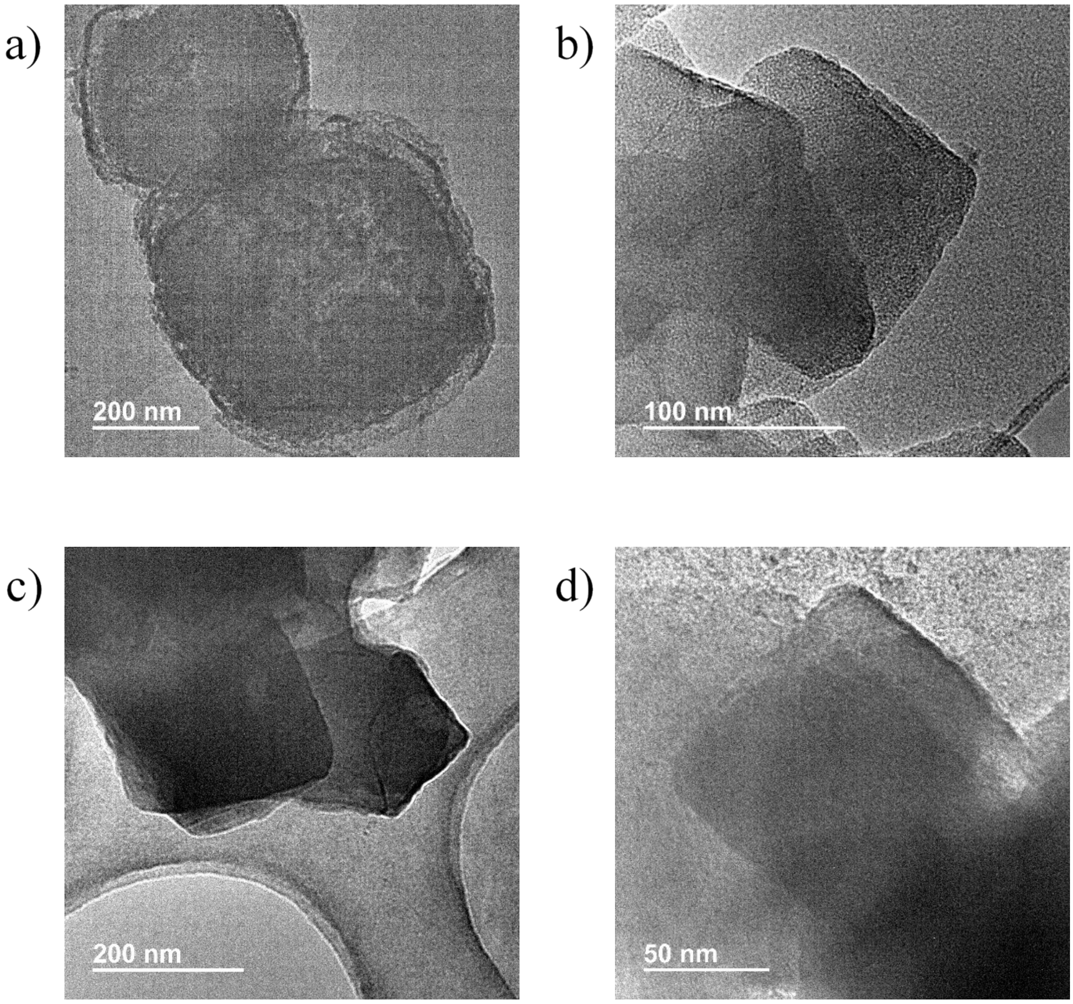

Figure S13. Representative TEM images of MIL-125(Ti)-NH_2 (a), UiO-66(Zr)-NH_2 (b), UiO-66(Zr)-H (c) and UiO-66(Zr)-NO_2 (d) materials.

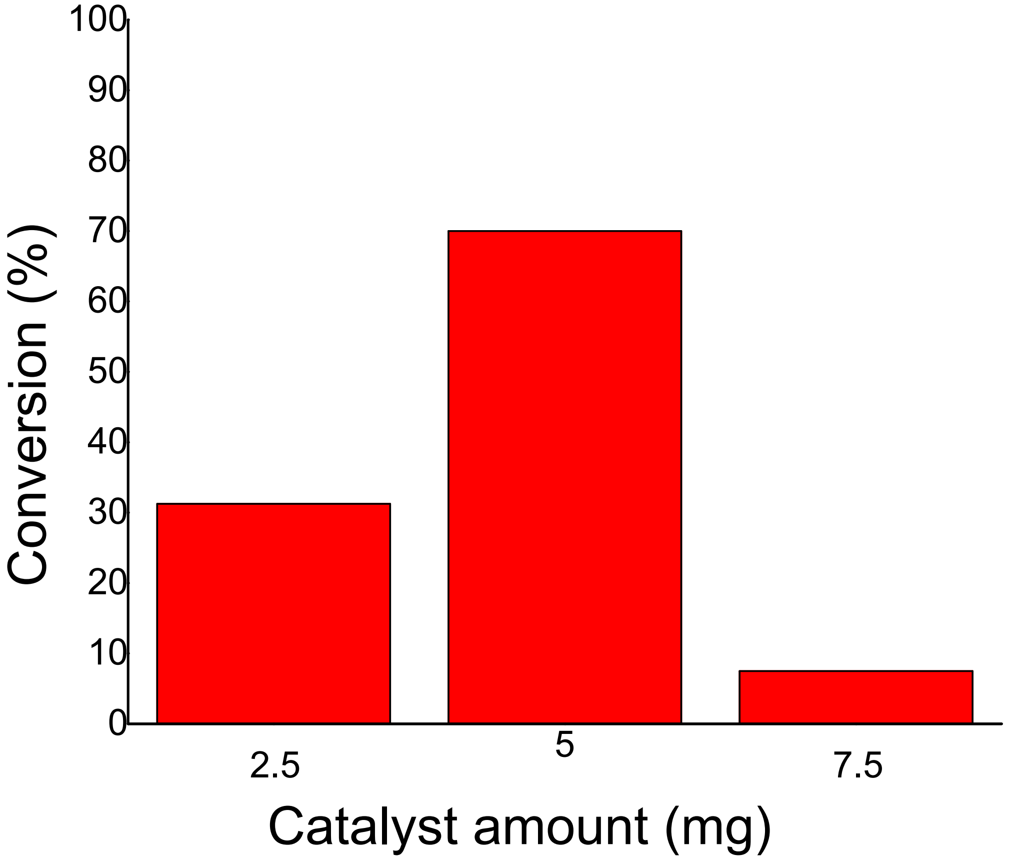

Figure S14. Photocatalytic reduction of 4-nitrophenol to 4-aminophenol under UV-Vis using different amounts of UiO-66(Zr)-NH_2 solid. Reaction conditions: Catalyst amount as indicated, p-nitrophenol (0.02 mmol), solvent (H_2O:MeOH, 1.25:1.25 mL), photoreactor volume (51 mL), Xe lamp (150 W), 50 ºC.

Table S2. Values of BET surface area before and after reaction of MOFs employed as bifunctional catalysts in this work.

Catalyst	Theoretical catalyst formula	BET surface area (m^2/g); before reaction	BET surface area (m^2/g); after thermal induced reaction	BET surface area (m^2/g); after photo induced reaction
MIL-125(Ti)-NH_2	$Ti_8O_8(OH)_4(C_6H_3C_2O_4NH_2)_6$	1200	1100	997
UiO-66(Zr)-H	$Zr_6O_4(OH)_4(OOC\text{-}C_6H_4\text{-}COO)_6$	1368	840	906
UiO-66(Zr)-NH_2	$Zr_6O_4(OH)_4(OOC\text{-}C_6H_3NH_2\text{-}COO)_6$	923	650	548
UiO-66(Zr)-NO_2	$Zr_6O_4(OH)_4(OOC\text{-}C_6H_3NO_2\text{-}COO)_6$	903	490	471